Tutorial: Molecular structures and MD of small and larger molecules using DFTB+

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How to connect to Lired:

1. ssh sirle@lired.iacs.stonybrook.edu
2. Password: DFTBwork
3. You should see prompt “[sirle@lired ~]$
4. Create your own directory, e.g. “mkdir joe” where joe is the directory you will run calculations in
5. cd “joe”

How to visualize .xyz data files:

a) MOLDEN
b) JMOL
c) …

Short instructions for important UNIX commands (I):

General UNIX commands:

cd <dir>	change directory to <dir>
cd ..	Go back one directory
ls	list files in current directory
vi <file>	view and edit file <file> (gedit is also available)
cp <file> <new>	copy file <file> to file <new>
mkdir <dir>	create directory <dir>

(ask your friends for help if you are lost at any time)

Short instructions for important UNIX commands (II):

Important commands:

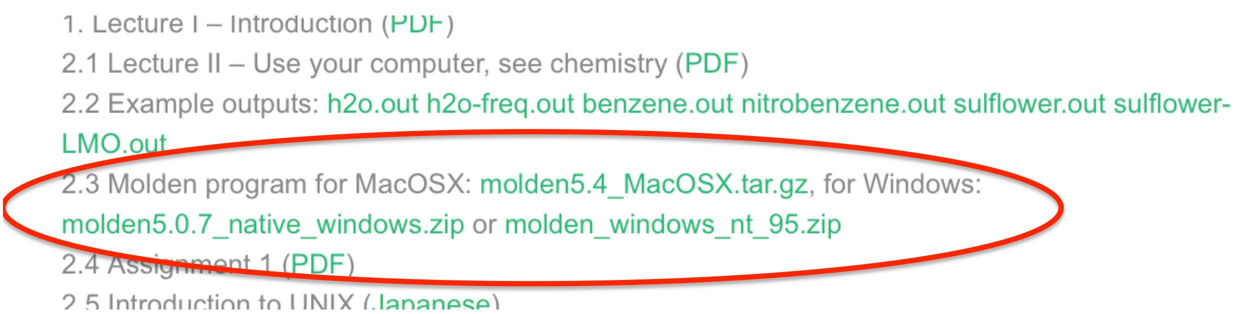
dftb+	(the DFTB+ program)
waveplot	(plotting molecular orbitals, electron densities, etc.)
gnuplot	(the gnuplot program)

Visualization: DFTB+ produces .xyz files which can be viewed with MOLDEN or JMOL or …

To install MOLDEN on your computers, open:
http://qc.chem.nagoya-u.ac.jp

Click on “Teaching”

You will see:

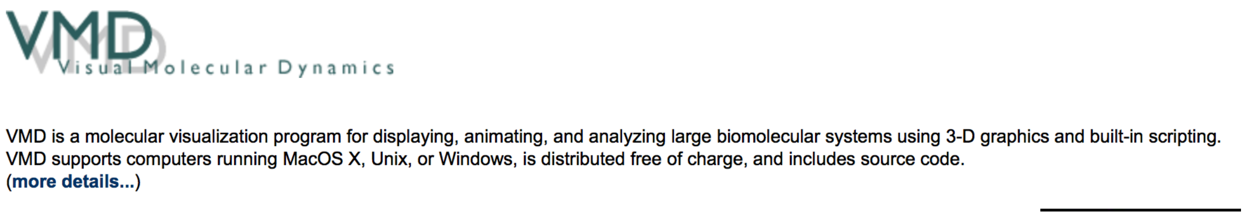


1. Lecture I – Introduction (PDF)
2.1 Lecture II – Use your computer, see chemistry (PDF)
2.2 Example outputs: h2o.out h2o-freq.out benzene.out nitrobenzene.out sulflower.out sulflower-LMO.out
2.3 Molden program for MacOSX: molden5.4_MacOSX.tar.gz, for Windows: molden5.0.7_native_windows.zip or molden_windows_nt_95.zip
2.4 Assignment 1 (PDF)
2.5 Introduction to UNIX (Japanese)

To download, you are asked to provide a userid and password.

Userid: qcguest
Password: qcigf! (quantum chemistry is great fun!)

For visualization of molecular orbitals or densities, you can use VMD or any other software that can plot Gaussian ‘s “cube” files



VMD Visual Molecular Dynamics

VMD is a molecular visualization program for displaying, animating, and analyzing large biomolecular systems using 3-D graphics and built-in scripting. VMD supports computers running MacOS X, Unix, or Windows, is distributed free of charge, and includes source code.
(**more details...**)

http://www.ks.uiuc.edu/Research/vmd/

Directories on the server

The following directory structure exists with corresponding inputs for DFTB+ in our home directory /gpfs/home/sirle:

Directory	Description
H2O	Water molecule geometry optimization
formamide	input for formamide rotational barrier calculation
benzene	benzene molecular geometry optimization
C60	C_{60} geometry optimization
nanotube	(5,5) nanotube geometry optimization
Fe38	Fe38 geometry optimization
C82	single point calculation for MO visualization
Sc2C2C82	single point calculation for MO visualization
MD	water NVE/NVT BOMD simulations

Frequently occurring problems

The location of the DFTB parameter files has to be specified in the `dftb_in.hsd` input file. If the specified directory does not exist or the parameter files do not exist, the program will stop with an error message. The parameter files are stored in the directory

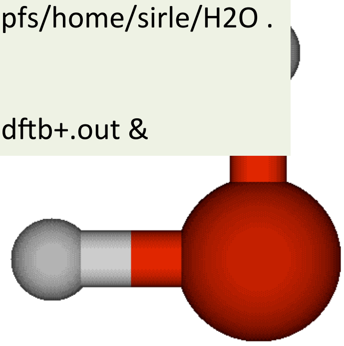
/gpfs/home/sirle/SKfiles

The default maximum number of geometry updates during geometry optimization is 200. You may have to change this to converge your geometries by setting MaxSteps = 300 (a number larger than 200) in the Driver{} Section of `dftb_in.hsd`

1a) H2O single point calculation (input)

Necessary commands:

```
cd joe
cp –r /gpfs/home/sirle/H2O .
cd H2O
Ls
dftb+ > dftb+.out &
```



Geometry file:

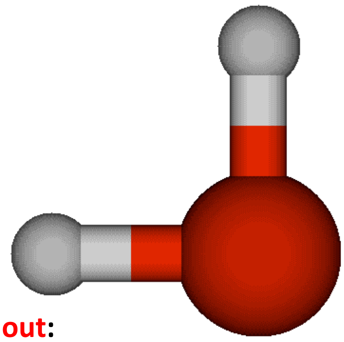
h2o.gen:

```
3 C
O H
1 1  0.0 0.0 0.0
2 2  1.0 0.0 0.0
3 2  0.0 1.0 0.0
```

dftb_in.hsd:

```
Geometry = GenFormat {
 <<< "h2o.gen"
 }
 Driver = {}
 Hamiltonian = DFTB{
   Charge = 0
   SpinPolarisation{}
   SCC = Yes
   SCCTolerance = 1e-6
   MaxSCCIterations = 100
   Mixer = Broyden{}
   MaxAngularMomentum = {
     O = "p"
     H = "s"
  }
  SlaterKosterFiles = Type2FileNames {
    Prefix = "/gpfs/home/sirle/SKfiles/"
    Separator = "-"
    Suffix = ".skf"
    LowerCaseTypeName = No
  }
 }
```

1a) H2O single point calculation (output)



detailed.out:

```
Net atomic charges (e)
 Atom      Net charge
   1     -0.56908879
   2      0.28454439
   3      0.28454439
```

```
Eigenvalues /eV
 -23.02217599
 -10.69768502
  -9.04017641
  -7.06500997
   7.80946767
  13.40675941
```

```
Fillings
   2.00000
   2.00000
   2.00000
   2.00000
   0.00000
   0.00000
```

dftbp.out:

```
*******************************************************************************
** Geometry step: 0
*******************************************************************************

 iSCC Total electronic   Diff electronic     SCC error
   1  -0.41146057E+01   0.00000000E+00   0.77431585E+00
   2  -0.41189864E+01  -0.43807053E-02   0.56529143E+00
   3  -0.41241083E+01  -0.51219356E-02   0.62694765E-02
   4  -0.41241090E+01  -0.64734819E-06   0.72216815E-04
   5  -0.41241090E+01  -0.85880636E-10   0.52564193E-08
>> Charges saved for restart in charges.bin

 Total Energy:                    -4.0698274647 H
 Total Mermin free energy:         -4.0698274647 H
```

1b) H2O geometry optimization

Necessary commands:

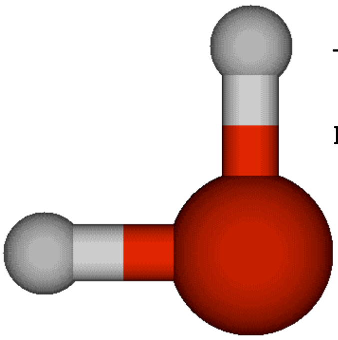
```
vi dftb_in.hsd
(or gedit dftb_in.hsd)
dftb+ > dftb+.out &
```

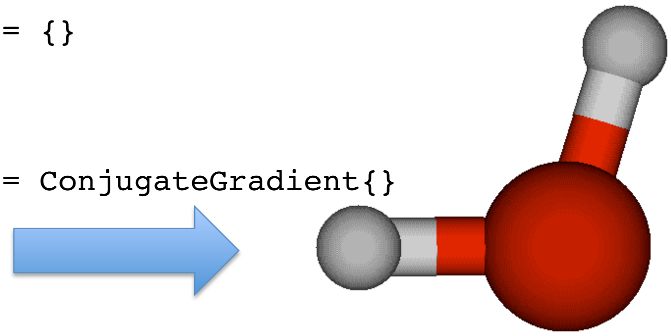
Edit the dftb_in.hsd file using the vi command, and change the line:

```
Driver = {}
```

To:

```
Driver = ConjugateGradient{}
```





Task: Use MOLDEN to check bond lengths and angles before and after optimization

Command: molden geo_end.xyz

Initial geometry:

```
Total Energy:                 -4.0698274647 H
Total Mermin free energy:         -4.0698274647 H
Maximal force component:            0.466498E-01
```

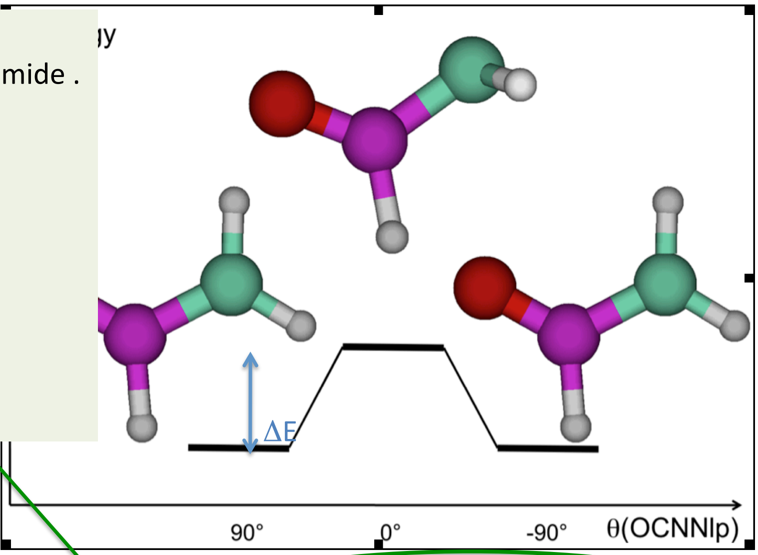
Optimized geometry, 14 geom. updates:

```
Total Energy:                 -4.0779379339 H
Total Mermin free energy:         -4.0779379339 H
Maximal force component:            0.873636E-06
```

1c) rotational barrier in formamide

Necessary commands:

```
cp -r /gpfs/home/sirle/formamide .
ls
cd formamide/planar
dftb+ > dftb+.out &
<record final energy>
molden geo_end.xyz
cd ../cd TS
dftb+ > dftb+.out &
<record final energy>
molden geo_end.xyz
```



Transition state geometry (TS):

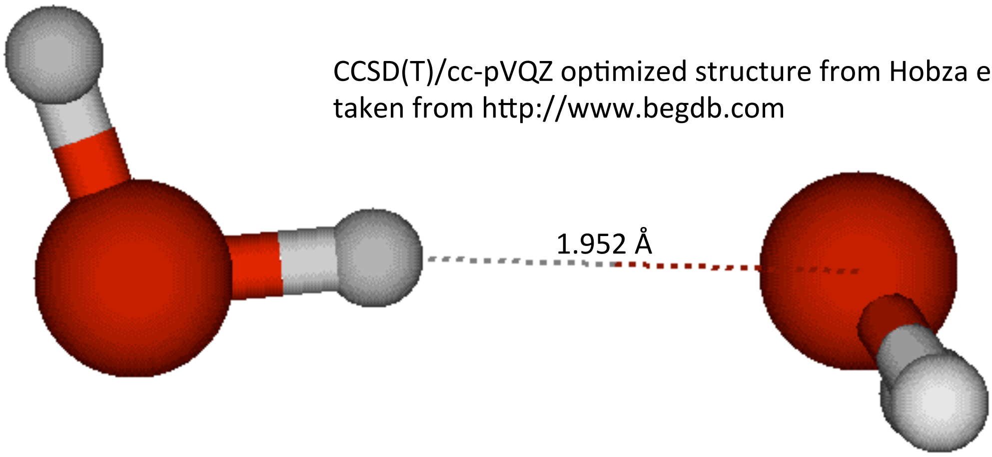
```
Total Energy:                 -8.5123283430 H
Total Mermin free energy:         -8.5123283430 H
Maximal force component:            0.448038E-04
```

Minimum geometry (planar):

```
Total Energy:                 -8.5347931959 H
Total Mermin free energy:         -8.5347931959 H
Maximal force component:            0.686719E-04
```

ΔE=-8.5123283430 - -8.5347931959 ha = -.0224648529 ha = 14.1 kcal/mol

1d-1) water dimer geometry optimization



CCSD(T)/cc-pVQZ optimized structure from Hobza et al.
taken from http://www.begdb.com

Task: Make appropriate input by yourself using H2O optimization (task 1b).

Compute SCC-DFTB binding energy BE = -[E_{dimer} – 2*$E_{monomer}$]
For this conformation: Edimer = -8.1611635663 ha
BE = -[-8.1611635663 – 2*(-4.0779379339)] ha = .0052876985
= 3.3 kcal/mol

Slater-Kirkwood dispersion term for SCC-DFTB*

*Elstner, M. *et* al., J. *Chem. Phys.*,**114**, 5149-5155, (2001).

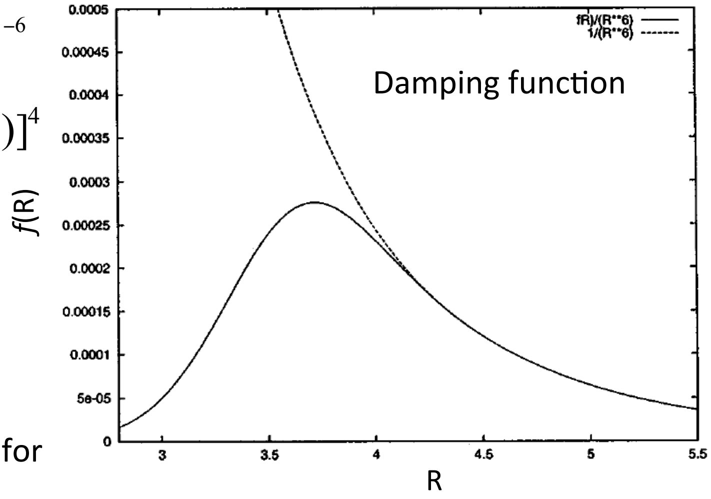
$$E_{dis}(R_{\alpha\beta}) = -\sum_{\alpha\beta} f(R_{\alpha\beta}) C_6^{\alpha\beta} (R_{\alpha\beta})^{-6}$$

$$f(R_{\alpha\beta}) = [1 - \exp(-3(R_{\alpha\beta}/R_0)^7)]^4$$

$$C_6^{\alpha\beta} = \frac{2C_6^{\alpha} C_6^{\beta} p_\alpha p_\beta}{p_\alpha^2 C_6^{\alpha} + p_\beta^2 C_6^{\beta}}$$

$$C_6^{\alpha} = 0.75\sqrt{N_\alpha p_\alpha^3}$$

p_α: polarizability (different values for different hybrid states of atoms)
R_0: cufoff distance
N_α: effective number of electrons



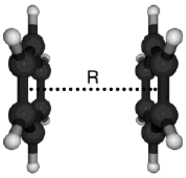
Available for C, H, N, O, P (only PO_4), and S (not SO_2)

Pauli repulsion

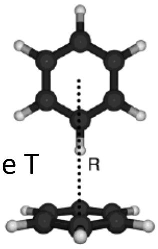
~ $1/R^6$ behavior

1d-2) Dispersion interaction: benzene dimer

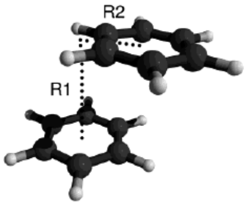
```
benzene/inputs> ls
benzene-disp   benzene-nodisp   PD-disp   S-disp   T-disp
```



Sandwich S



T-shape T



Parallel-displaced PD

Task 1:
optimize benzene monomer with and without dispersion interaction; what differences do you observe?

Task 2: Using dispersion interaction, optimize S, PD, and T dimer structures and compare your energies with literature values:

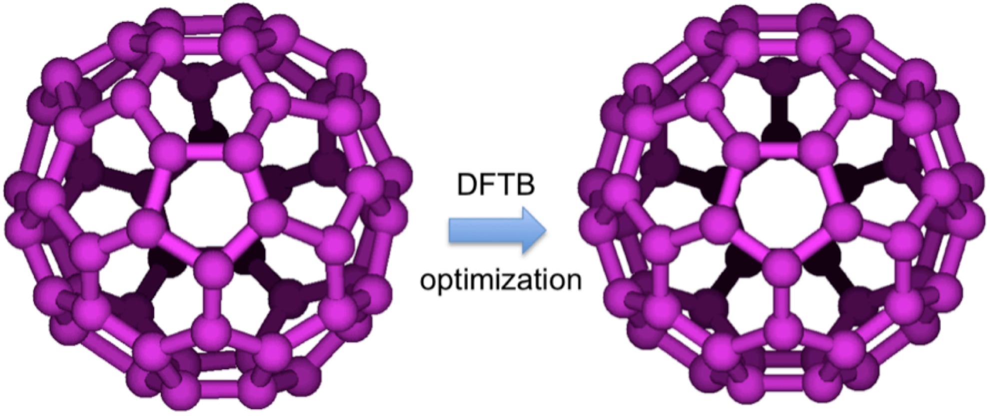
	S	T	PD	
BE	1.65	2.69	2.67	[kcal/mol]

Note that DFTB-D interactions are in the range 3-5 kcal/mol.

2a) C_{60} geometry optimization

Directory: C60

From T_n=2000K MD simulation



Initial geometry:
Total Energy: -103.1220165514 H
Total Mermin free energy: -103.1220165514 H
Maximal force component: 0.639238E-01

Optimized geometry, 18 geom. updates:
Total Energy: -103.2321663552 H
Total Mermin free energy: -103.2321663552 H
Maximal force component: 0.693582E-04

SCC-DFTB w/fractional orbital occupation numbers

Fractional occupation numbers f_i of Kohn-Sham eigenstates replace integer n_i

TB-eigenvalue equation $$\sum_{\nu} c_{\nu i}\left(H_{\mu\nu} - \varepsilon_i S_{\mu\nu}\right) = 0$$

$$E_{tot} = 2\sum_i f_i \varepsilon_i + E_{rep} + \frac{1}{2}\sum_{\alpha\beta}\gamma_{\alpha\beta}\Delta q_\alpha \Delta q_\beta$$

Finite temperature approach (Mermin free energy E_{Mermin})

M. Weinert, J. W. Davenport, *Phys. Rev. B* **45**, 13709 (1992)

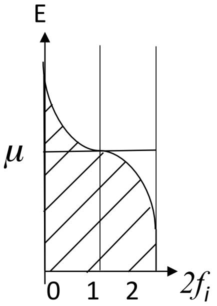
$$f_i = \frac{1}{\exp\left[\left(\varepsilon_i - \mu\right)/k_B T_e\right] + 1}$$

T_e: electronic temperature
S_e: electronic entropy

$$0 \le f_i \le 1$$

$E_{Mermin} = E_{tot} - T_e S_e$

$$S_e = -2k_B \sum_i^{\infty} f_i \ln f_i + \left(1 - f_i\right)\ln\left(1 - f_i\right)$$



Atomic force

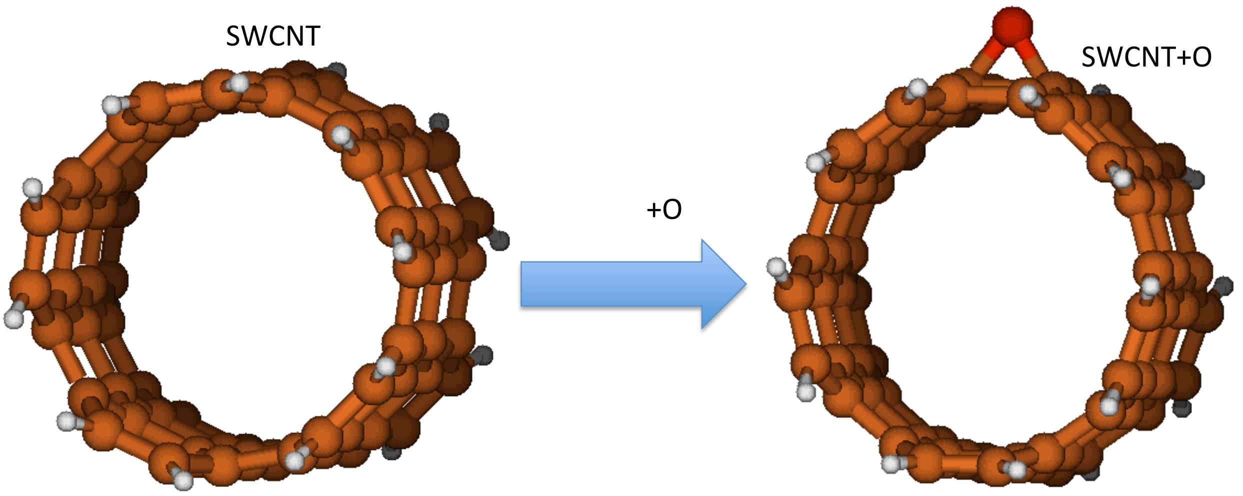
$$\vec{F}_\alpha = -2\sum_i f_i \sum_{\mu\nu} c_{\mu i} c_{\nu i}\left[\frac{\partial H^0_{\mu\nu}}{\partial \vec{R}_\alpha} - \left(\varepsilon_i - \frac{H^1_{\mu\nu}}{S_{\mu\nu}}\right)\frac{\partial S_{\mu\nu}}{\partial \vec{R}_\alpha}\right] - \Delta q_\alpha \sum_\xi^N \frac{\partial \gamma_{\alpha\xi}}{\partial \vec{R}_\alpha}\Delta q_\xi - \frac{\partial E_{rep}}{\partial \vec{R}_\alpha}$$

2b) Oxidation of (5,5) SWCNT

Directories: nanotube/inputs/pristine & oxidized & o_atom

Important: Need to use electronic temperature T_e = 1000 K or similar to obtain SCC convergence

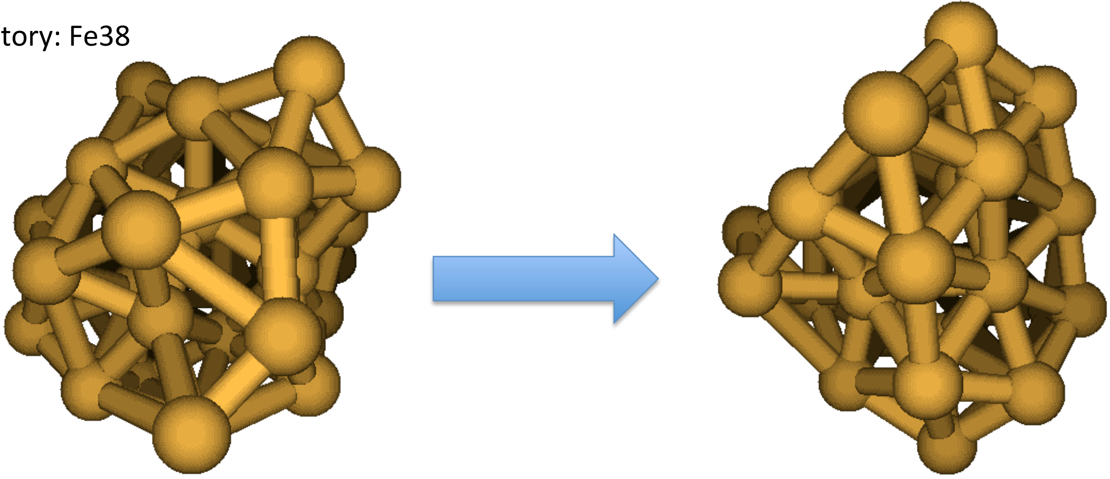
O Atom: SCC-DFTB energy: -3.0982859370 ha
SWCNT: optimized SCC-DFTB energy: -128.1960247645 ha
Oxidized SWCNT: optimized SCC-DFTB energy: -131.4584



Binding energy BE = -[E(SWCNT+O) – E(SWCNT) – E(O)] = 103.0 kcal/mol

2c) Fe38 geometry optimization

Directory: Fe38



Initial geometry:
Total Energy: -55.2723102833 H
Total Mermin free energy: -55.7289532045 H
Maximal force component: 0.736021E-01

Optimized geometry, T_e=1500K, 144 geom. updates:
Total Energy: -55.6471927268 H
Total Mermin free energy: -56.0689013490 H
Maximal force component: 0.575369E-04

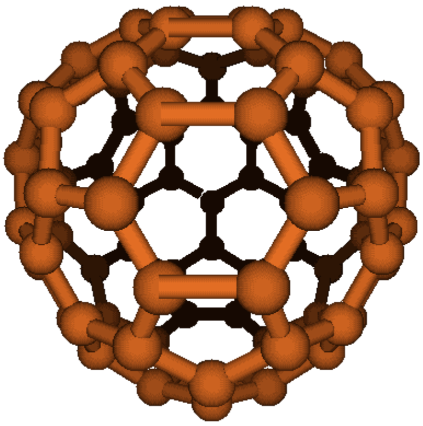
2d) MO plots of C_{82} and $Sc_2C_2@C_{82}$

Directories: **C82** and **Sc2C2C82**, subdirectories input and input/orbital in both
Important: Need to use electronic temperature T_e = 1000 K or similar to obtain SCC convergence

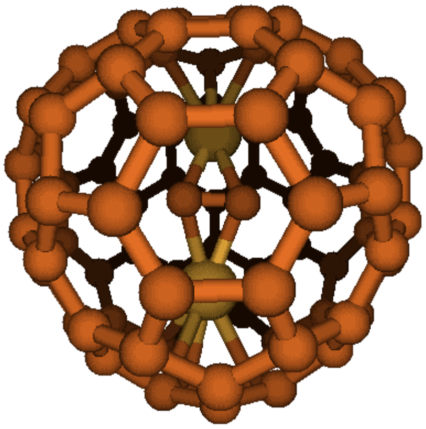
Write MO's in dftb_in.hsd:

```
Options = {
  WriteDetailedXML = Yes
  WriteEigenvectors = Yes
}
```

Bonus: Calculate binding energy of C2 and Sc atoms:
BE = -[E(Sc2C2@C82) – E(C82) – 2E(Sc) – E(C2)]



C82

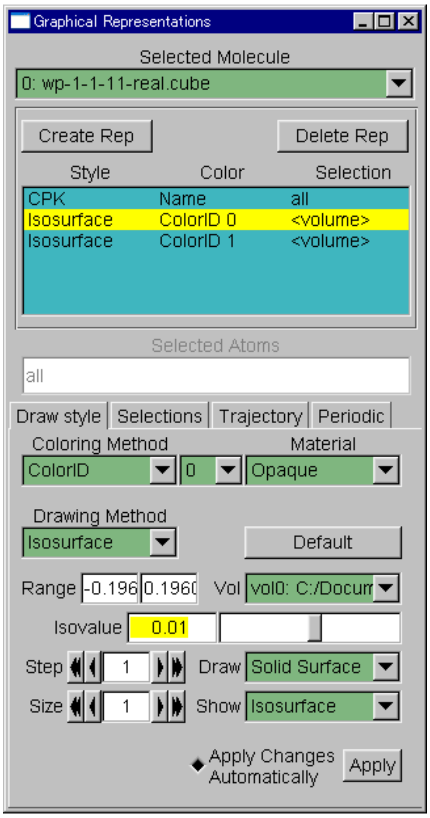


Sc2C2@C82

Sample “waveplot_in.hsd”

```
# General options

Options = {
  TotalChargeDensity = Yes        # Total density be plotted?
  TotalChargeDifference = Yes     # Total density difference plotted?
  ChargeDensity = Yes             # Charge density for each state?
  RealComponent = Yes             # Plot real component of the wavefunction
  PlottedSpins = { 1 -1 }
  PlottedLevels = { 11 14 15 16 17 18 }# Levels to plot
  PlottedRegion =  OptimalCuboid {}   # Region to plot

  NrOfPoints = { 50 50 50 }        # Number of grid points in each direction
  NrOfCachedGrids = -1             # Nr of cached grids (speeds up things)
  Verbose = Yes                    # Wanna see a lot of messages?
}

DetailedXML = "detailed.xml"        # File containing the detailed xml output of DFTB+
EigenvecBin = "eigenvec.bin"        # File cointaining the binary eigenvecs

# Definition of the basis
Basis = {
  Resolution = 0.01
  # Including mio-0-1.hsd. (If you use a set, which depends on other sets,
  # the wfc.*.hsd files for each required set must be included in a similar
  # way.)
  <<+ "wfc.mio-0-1.hsd"
}
```

Visualize the MOs with VMD



Selected Molecule: 0: wp-1-1-11-real.cube

Style	Color	Selection
CPK	Name	all
Isosurface	ColorID 0	<volume>
Isosurface	ColorID 1	<volume>

Selected Atoms: all

Coloring Method: ColorID 0

Material: Opaque

Drawing Method: Isosurface

Range -0.196 0.1960 Vol vol0: C:/Docum

Isovalue 0.01

Step 1 Draw Solid Surface

Size 1 Show Isosurface

◆ Apply Changes Automatically

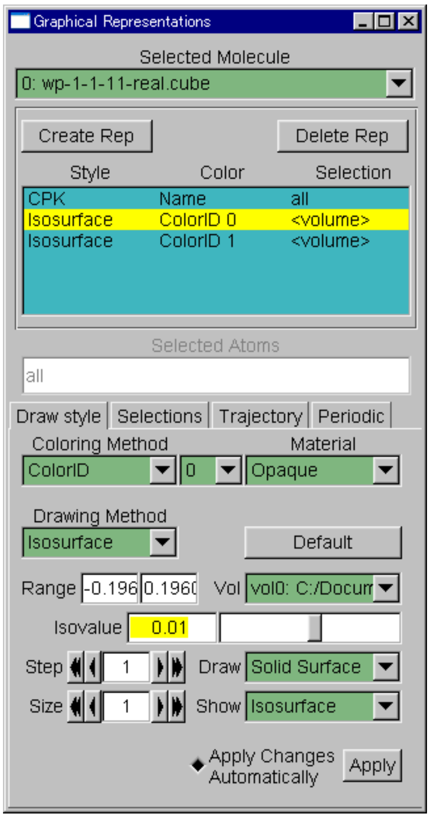
Note: Run these commands on your Terminal!

- Start VMD: Run All Programs/University-of-Illinois/ VMD/VMD 1.8.7
- File →New Molecule, then load the the desired cube file from (follow the procedure below)

-Browse
-My computer
-Z: drive (long name with Z: at the end, double-click)
-terminal_<color>_<M> (see label on your terminal)
-C82 (or Er2C2C82) (double-click)
-input (double-click)
-orbital (double-click)
-select desired cube file

Note: the location of your files will depend on the directory in which you ran the DFTB+ and waveplot programs

Visualize the MOs with VMD



Selected Molecule: 0: wp-1-1-11-real.cube

Style	Color	Selection
CPK	Name	all
Isosurface	ColorID 0	<volume>
Isosurface	ColorID 1	<volume>

Selected Atoms: all

Coloring Method: ColorID 0

Material: Opaque

Drawing Method: Isosurface

Range -0.196 0.1960

Vol vol0: C:/Docum

Isovalue 0.01

Step 1

Draw Solid Surface

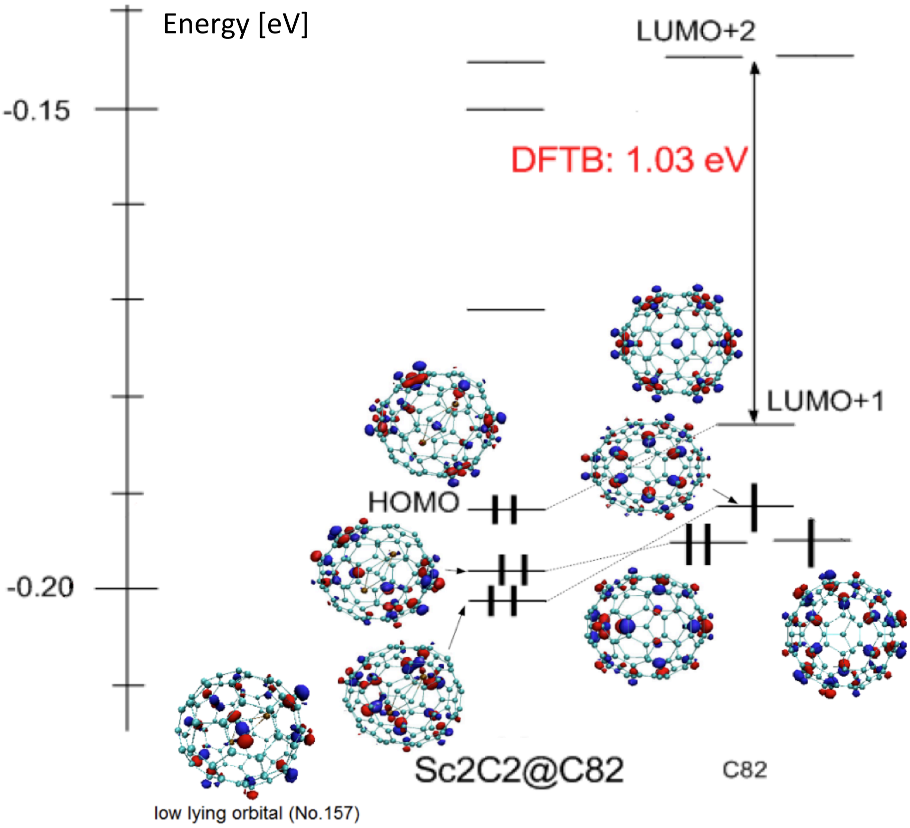
Size 1

Show Isosurface

◆ Apply Changes Automatically

- Graphics →Representations, then choose the drawing method (here CPK)
- Push the “Create Rep” button
- Change the drawing method “Isosurface”, then change the draw type from Points to Solid surfaces and show type to Isosurface
- Change the coloring method from Name to Color ID (color 0:blue)
- Set the Isovalue (positive number; for example, 0.01 etc.)
- Perform the same thing for negative Isovalue (for example, -0.01, color 1: red)

2d) MO plots of C_{82} and $Sc_2C_2@C_{82}$

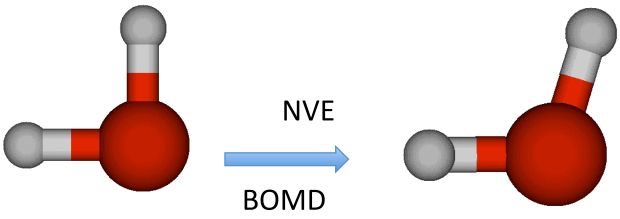


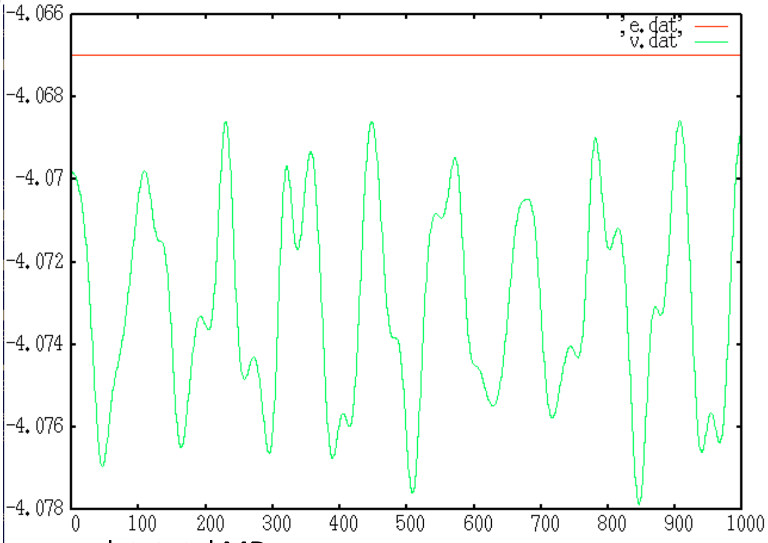
3a) H2O NVE SCC-DFTB/MD simulation

Directory: MD/NVE

dftb_in.hsd:

```
Geometry = GenFormat {
 <<< "h2o.gen"
 }
 Driver = VelocityVerlet{
  Steps = 999
  TimeStep [Femtosecond] = 0.10
  Thermostat = None {
    InitialTemperature [Kelvin] = 298
  }
 OutputPrefix = "geo_stp"
 }
 Hamiltonian = DFTB{
    Charge = 0
    SpinPolarisation{}
    SCC = Yes
    SCCTolerance = 1e-6
    MaxSCCIterations = 100
    Mixer = Broyden{}
    MaxAngularMomentum = {
       O = "p"
       H = "s"
  }
SlaterKosterFiles = {
    O-O = "../SKfiles/O-O.skf"
    O-H = "../SKfiles/O-H.skf"
    H-O = "../SKfiles/H-O.skf"
    H-H = "../SKfiles/H-H.skf"
  }
 }
```

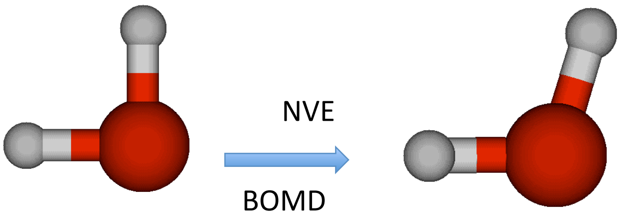




e.dat: total MD energy
v.dat: MD potential energy

3a) H2O NVE SCC-DFTB/MD simulation

dftb_in.hsd:



```
T: grep "Kinetic Energy:" md.out |awk '{print $4}' > t.dat
V: grep "Potential Energy:" md.out |awk '{print $3}' > v.dat
E: grep "Total MD Energy:" md.out |awk '{print $4}' >
e.dat
```

E = T + V

E is conserved in NVE (microcanonical) simulations

Visalization in gnuplot:

```
Type “gnuplot”
gnuplot> set style data lines
plot ‘v.dat’,’e.dat’
plot ‘t.dat’
exit
```

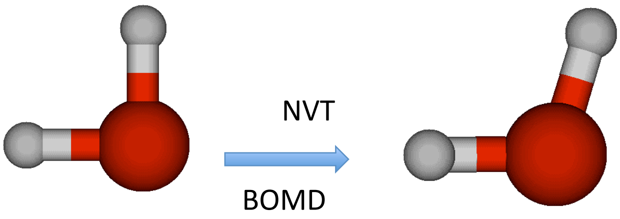
Interpret your results. How are T and V related?

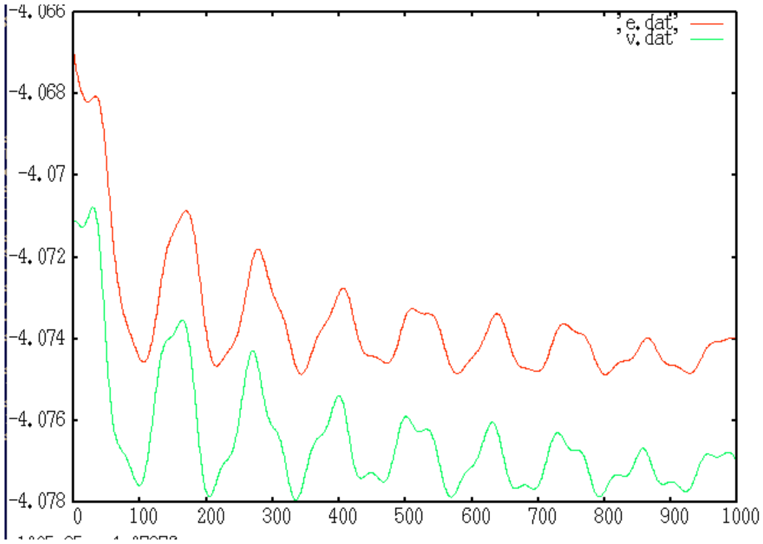
3b) H2O NVT SCC-DFTB/MD simulation

Directory: MD/NVT

dftb_in.hsd:

```
Geometry = GenFormat {
 <<< "h2o.gen"
 }
 Driver = VelocityVerlet{
  Steps = 999
  TimeStep [Femtosecond] = 0.10
  Thermostat = Berendsen {
    Temperature [K] = 298.0
    CouplingStrength = 0.1
  }
  Velocities [AA/ps] = {
   <<< "VELOC.DAT"
 }
 OutputPrefix = "geo_stp"
 }

 Hamiltonian = DFTB{
    Charge = 0
    SpinPolarisation{}
    SCC = Yes
    SCCTolerance = 1e-6
    MaxSCCIterations = 100
    Mixer = Broyden{}
    MaxAngularMomentum = {
       O = "p"
       H = "s"
  }
SlaterKosterFiles = {
    O-O = "../SKfiles/O-O.skf"
    O-H = "../SKfiles/O-H.skf"
    H-O = "../SKfiles/H-O.skf"
    H-H = "../SKfiles/H-H.skf"
  }
 }
```

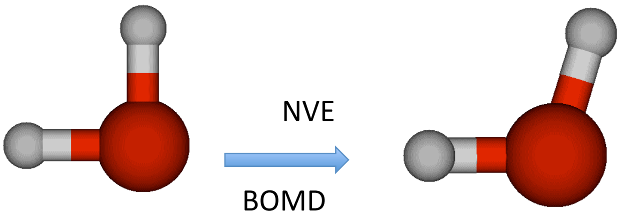




e.dat: total MD energy
v.dat: MD potential energy

3b) H2O NVT SCC-DFTB/MD simulation

dftb_in.hsd:



E is NOT conserved in NVT simulations, but T is:
½ $mv^2 = 3/2k_bT$

$$\delta = \left[1 + \frac{\Delta t}{\tau_T}\left\{\frac{T_0}{T(t-\Delta t)} - 1\right\}\right]^{1/2} \quad , \quad v_i = \delta v_i$$

In case of one water molecule, 1 au = 105258.2 K

awk '{print $1*105258.2}' t.dat > temp.dat

Interpret your results. Try different values of the coupling constant τ_T.
What is the influence of τ_T?